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MICROPARACRYSTALLINE MODEL FOR MEDIUM-RANGE ORDER IN NON-CRYSTALLINE CHALCOGENIDES

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The medium range order in disordered chalcogenides has been explained by the existence of reminiscent crystal-like configurations with distorted arrangement of the atoms. Using the paracrystalline theory, two parameters have been defined for the characterization of the MRO in glass: paracrystallite thickness and paracrystallite distortion.

1. Introduction

One of the most important problems in the physics of amorphous materials in general and non-crystalline chalcogenides in particular is the structure at the atomic scale. The extent of the order in a disordered material is still a subject of controversy [1].

The short-range order (SRO) in a given solid is related to the chemical bonding. Therefore, a profound similarity does exist between the SRO in crystalline and non-crystalline state of the same compound.

The medium-range order (MRO) or intermediate-range order (IRO) is defined by the correlation between the positions of the atoms in the range $0.5 - 1$ nm, in excess of those expected for an ideal Zachariasen-type continuous random network characterized by a random dihedral angle distribution [2].

It is very unlikely that a detailed physical theory will be developed to relate all macroscopic properties of glass with atomic processes without providing practical means of defining atomic geometry.

The "signature" of MRO in covalently bonded glasses is the first sharp diffraction peak (FSDP) or pre-peak in the X-ray diffraction pattern, $I(Q)$. The intensity, half-width and position of this peak on the scale of the scattering vector, Q, are characteristic for every material. The FSDP of an amorphous solid exhibits high sensitivity against temperature, pressure, aggregation state, etc. [3-5].

The FSDP is situated at low Q values ($1.0 - 1.5$ Å^{-1}) and arises probably from correlation at distances of $4.5 - 6.0$ Å rather than from simple nearest or next nearest neighbours.

In this paper we discuss the X-ray diffraction features of several amorphous solids exhibiting FSDP, with special emphasis on non-crystalline chalcogenides, in the frame of a new model based on the paracrystalline theory of Hosemann [6], proposed for disordered materials.

2. Structural models for medium-range order

Careful analysis of the X-ray diffraction patterns in many amorphous and glassy materials has shown that FSDP is a widely observed feature (e.g. in a-As [7], a-SiO$_2$ [8], a-As$_2$Se$_3$ [9]) but not universal (e.g. FSDP is lacking in a-Si [10]). This particular feature of many non-crystalline solids aroused much speculation as to its origin in real space.

Four main models for the atomic scale configuration, that determine the special aspects of MRO in amorphous solids, were developed up to day.

a) Microcrystalline model

The model was applied firstly to amorphous As_2S_3. Leadbetter and Apling [11] have calculated the correlation functions in real and wave vector space for small randomly oriented fragments of crystal structure. The agreement between the model and experiment was found to be poor. The strongest discrepancy in the radial distribution curves is related to the strong peak at about 4.5 Å, due to cross ring correlations in the crystal, which are absent in the experimental functions.

b) Layered model

As an alternative, the experimental results on the same a-As_2Se_3 were interpreted in the frame of a structure with disordered layers [3,12].

The fundamental evidence for layers in a-As_2S_3 was the presence of the FSDP and its near coincidence with the (020) reflection of the crystal. A layer is defined as two or more sheets or roughly parallel and planar atom groupings, which are bound mainly by non-bonded forces. In this model, the non-bonded interactions, i.e. interlayer correlations, give rise to the FSDP. The definition of the layer does not exclude single sheets of atoms wrapped over each other. Because the layers can be appreciably cross-linked by chemical bonds the structure approaches that of a cluster and, therefore, an ambiguous interpretation of FSDP cannot be avoided.

c) Clustered model

A cluster is defined as a group of atoms (in general greater than six) constrained to a particular internal geometry by chemical bonds. Clusters can be either chemically bonded within the main structure or packed randomly and held together by non-bonded forces. The first clustered model was developed by Phillips [13] and is represented by condensation of the so-called "outrigger rafts".

In the clustered model the MRO is expressed as intra-cluster correlations and from this order appears FSDP.

Nevertheless, the major difficulty with clusters (especially big cluster ~ 20 atoms, as e.g. "outrigger rafts") is that they introduce too much medium-range order. To overcome this difficulty the clusters must be distorted but this implies a serious problem of stability.

d) Void correlation model

Fowler and Elliott [14] gave arguments to support the conclusion that FSDP is due to contributions of Fourier components from a broad region of the real space (including e.g. a density deficit at about 4.5 Å in the case of a-As_2S_3), rather than a distinct structural feature. They speculated that the presence of lone pairs in the amorphous solid, rather than clusters could cause such a density deficit. After Fowler and Elliott [14] lone pairs strongly repel each other and, therefore, force a structure to become more open, especially if the structure is disordered. The presence of lone pairs (absent in a-Si) forces an expansion of the average ring size, with the concomitant deficit in inter-atomic correlations near 4.5 Å, necessary for the observation of FSDP.

According to the void correlation model [15] FSDP is a chemical order pre-peak due to interstitial volume around cation centered structural units. The calculated positions of FSDP for some covalent glasses (SiO_2, GeO_2, $ZnCl_2$, $GeSe_2$) agree well with the experiment and the temperature and pressure dependencies of the FSDP can be, thus, explained in terms of density effects.

Although successful in many instances, the model cannot explain satisfactorily the difference in behaviour of the FSDP when the glass is subjected to uniaxial compression and when hydrostatic compression is applied. In both cases the peak intensity decreases [16].

All the above-described models fail to account for all details of I(Q) function. In general only FSDP or FSDP + main diffraction peak are examined in order to establish the validity of a model.

3. Paracrystallinity and the microparacrystalline model

The paracrystalline theory developed by Hosemann [6] and formerly applied to fibers, stems from the idea that the non-crystalline solid consists from crystalline, distorted configurations, that are preserved during crystal-amorphous or crystal-melt transition. These configurations are quasi-aligned in the disordered matrix. The general structure based on paracrystallites gives rise to an X-ray

diffraction pattern similar to that corresponding to a multilayer structure. First order intense peak is followed by higher diffraction order peaks with rapidly decreasing intensity.

Hindeleh and Hosemann [17] found a very important relation between the peak width and the diffraction order. There exists a linear dependence between the width of the diffraction halos, δb, and the square of the quadratic sum of the Miller indices for the basical paracrystalline plane, (00h):

$$\delta b = 1/D + [(pgh)^2/d] \qquad (1)$$

In the case of layered structures, the basical layer plane can be assimilated to a (001) plane. The linear dependence $\delta b \sim f(h^2)$, where h is the diffraction order, is a strong argument for the existence of microparacrystallites as constituent elements of a given glass [18].

From the Hindeleh-Hosemann plot one can extract two important parameters. The intercept of the line with the ordinate gives the value 1/D, where D is the mean paracrystallite thickness normal to the paracrystalline base plane. From the slope of the right line one gets the paracrystalline distortion, g, as defined in the theory as the relative paracrystalline distance fluctuation:

$$g^2 = (\overline{d^2}/\overline{d}^2 - 1)^{1/2} \qquad (2)$$

where d is the net plane spacing, $\overline{d^2}$ is the mean of d^2 and $\overline{d}$ is the averaged d, that is the quasi-periodicity.

For the ideal crystalline structure g = 0 and for the complete disappearance of crystal-like structural features g = 1.

The application of the theory of paracrystallinity to catalysts, bio-polymers, fibbers, synthetic polymers, glasses and melts [19,20] led to an empirical relation of a new kind of equilibrium state:

$$N^{1/2} \cdot g = \alpha^* \qquad (3)$$

with $\alpha^* = 0.15 \pm 0.05$. N is the mean number of net-plane layers in a paracrystallite.

The equation 3 implies that there is a limit to the growth of paracrystal layers, N, depending on the magnitude of the paracrystalline distortion, g.

We must finally remark that, based on a wide range of data, Phillips [21] suggested that in vitreous SiO_2 there are clusters, which have the internal topology of cristobalite, a cubic structure of SiO_2 with density 5 % greater than vitreous SiO_2 and with the Si atoms arranged on a diamond lattice. The dominant surface structure of the cristobalite paracrystallites is expressed by (001) planes and the clusters are about 60 Å in diameter.

Taking into account the above discussed data, we developed a paracrystallite model for medium-range order, which was applied to vitreous SiO_2 and to a number of glassy chalcogenides.

In the case of chalcogenides, which are characterized by mean atomic coordinations between 2 and 3, the basical layers in crystals lose their intrinsic order by amorphization, but preserve the layer stacking along the distances of the order of paracrystallite thickness parameter. The type of structural element preserved in the glassy state seems to depend on the chemical composition of the material. The most stable structural planes of the corresponding crystalline phases are maintained in the disordered materials with ill-defined packing and they give rise to MRO structural effects. The existence of long-lived crystal-like clusters in melt, before quenching, leads to a lower free energy for gas-like + crystal-like configurations than for homogeneous gas-like atomic configuration [22].

Supposing the formation of paracrystallites in bulk chalcogenide glasses it is possible to treat the problem of medium-range order in the frame of the Hindeleh-Hosemann theory. Thus, after careful processing of the X-ray diffraction data, it is possible to get two parameters, which characterize the paracrystallites in the glass and, therefore, the atomic correlations: the paracrystallite thickness and the paracrystalline distortion.

4. Documented cases

We have applied the microparacrystalline model for medium-range order, firstly to vitreous SiO_2 and then to several representative glassy chalcogenides: $GeSe_2$, $AsS_{1.66}$ and As_2Se_3. Figure 1

shows the Hindeleh-Hosemann plot for vitreous SiO_2. From this plot the two MRO parameters were obtained: $D = 18.5$ Å and $g = 0.056$.
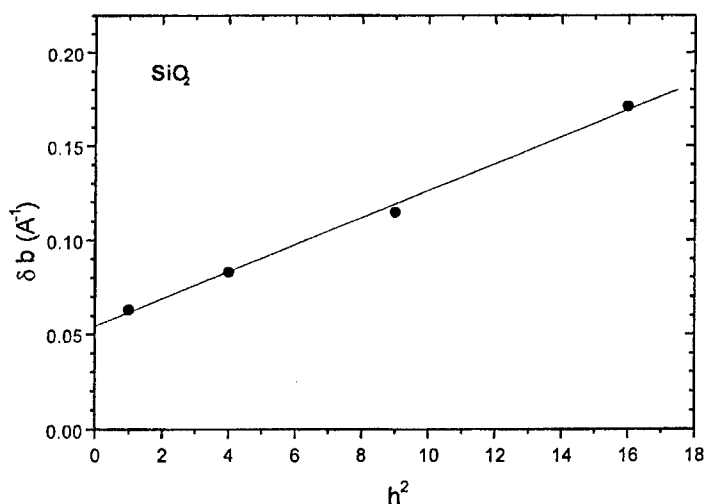

Fig. 1. Hindeleh-Hosemann plot for the determination of the paracrystallite
parameters D and g in vitreous SiO_2.

The paracrystalline clusters in glassy SiO_2, after Phillips [24], are extended over a distance of at least 25 Å. Cristobalite domains with size ~60 Å were observed from TEM by Zarzycki [21]. Meade et al. [25] reported a mean size of quasi-ordered configurations of ~20 Å. The distortion of the paracrystallite is enough low, if one compares our result with the value reported by Hosemann et al. [26]: $g = 0.15$.

The peaks in the X-ray diffraction diagrams of $GeSe_2$ and $AsS_{1.66}$ [27] have been carefully measured, in order to draw the Hindeleh-Hosemann plots (see Fig. 2 and 3). The results show for glassy $GeSe_2$: $D = 69.6$ Å and $g = 0.071$, and for $AsS_{1.66}$: $D = 26.6$ A and $g = 0.068$. While the paracrystalline distortion is nearly identical in both cases, the paracrystalline thickness differs considerably, and this is an interesting result. The values of D extracted from the width of FSDP and reported in the literature are 60 Å for $GeSe_2$ and 30 Å for As_2S_3 [28].
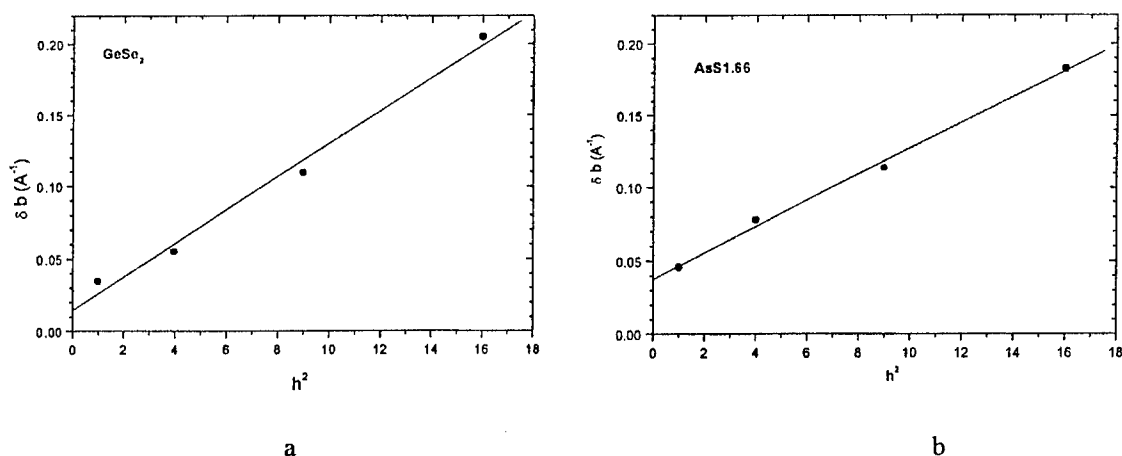

a   b

Fig. 2. The Hindeleh-Hosemann plot for the determination of the paracrystallite parameters in
glassy $GeSe_2$ (a) and $AsS_{1.66}$ (b).

Finally we analyzed the cases of As_2Se_3 chalcogenide when heated above the softening temperature ($T_g = 215$ °C) at 400 °C and at 630 °C [29]. It is well known that, during heating, and even in the molten state, the MRO tends to develop itself, as evidenced by the amplification of the FSDP intensity. Figure 4 shows the results.
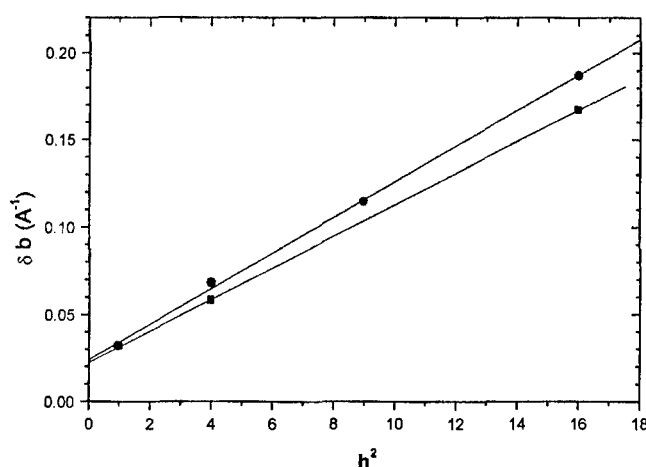
Fig. 3. The Hindeleh-Hosemann plot for an As_2Se_3 sample in the molten state at 400 °C (■)
and at 600 °C (●).

When the sample temperature is raised from 400 to 630 °C the paracrystallite thickness decreases from 45.1 to 42.1 Å and the paracrystalline distortion increases from 0.067 to 0.072. At the room temperature As_2Se_3 exhibit a D value of 30.4 Å [18] while g is 0.067. This discrepancy can be explained as follows. In the molten state few constraints are exerted on the disordered paracrystalline layers and, therefore, more relaxation is produced with the consequence of a better alignment of the layers. In the amorphous solid state the stacking of the disordered layers is more difficult to appear on a longer scale, because the constraint from the surrounding matrix is higher, and, therefore, the thickness of the paracrystallite is smaller.

5. Conclusions

A new model for medium-range order in non-crystalline chalcogenides has been introduced. The model is based on the old paracrystalline theory of Hosemann with one major amendment: the paracrystallites consist of the backbones of the original stable crystal corresponding to the chemical composition of the material (or crystal of the most approached composition), including as entities the planes of closest packed arrangement of the atoms. These planes represent the ultimate reminiscence of a crystal in the melt. For many chalcogenides these planes are not composed of ordered configuration of atoms as in the crystal, but are characterized by a disordered arrangement of atoms, reflected in the ring configuration with various number of atoms.

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